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[Title of the Document] CLAIMS

[Claim 1] A carbon fiber composite material comprising an elastomer and carbon nanofibers dispersed in the elastomer, wherein the elastomer has an unsaturated bond or a group, having affinity to the carbon nanofibers.

5 [Claim 2] The carbon fiber composite material as defined in claim 1, wherein the elastomer has an average molecular weight of 5,000 to 5,000,000.

[Claim 3] The carbon fiber composite material as defined in claim 1 or 2, wherein the elastomer has, in at least one of its main chain, side chains and terminal chains, at least one functional group selected from functional groups such as a double
10 bond, a triple bond, alpha-hydrogen, a carbonyl group, a carboxyl group, a hydroxyl group, an amino group, a nitrile group, a ketone group, an amido group, an epoxy group, an ester group, a vinyl group, a halogen group, an urethane group, a biuret group, an allophanate group and a urea group.

[Claim 4] The carbon fiber composite material as defined in any one of claims 1
15 to 3, wherein the elastomer has a spin-spin relaxation time (T_{2n}) of its network component of 100 to 3,000 microseconds in its uncrosslinked form as measured at 30°C by Hahn-echo method using pulsed NMR technique.

[Claim 5] The carbon fiber composite material as defined in any one of claims 1 to 3, wherein the elastomer has a spin-spin relaxation time (T_{2n}) of its network
20 component of 100 to 2,000 microseconds in its crosslinked form as measured at 30°C by Hahn-echo method using pulsed NMR technique.

[Claim 6] A carbon fiber composite material comprising an elastomer and carbon nanofibers dispersed in the elastomer, wherein the uncrosslinked elastomer has a first spin-spin relaxation time (T_{2n}) of 100 to 3,000 microseconds and a second
25 spin-spin relaxation time (T_{2nn}) of zero or 1,000 to 10,000 microseconds, the fraction (f_{nn}) of a component having the second spin-spin relaxation time being less than 0.2, as measured at 150°C by Hahn-echo method using pulsed NMR technique.

[Claim 7] A carbon fiber composite material comprising an elastomer and carbon nanofibers dispersed in the elastomer, wherein the crosslinked elastomer has a first spin-spin relaxation time (T_{2n}) of 100 to 2,000 microseconds and a second spin-spin relaxation time (T_{2nn}) is zero or 1,000 to 5,000 microseconds, the fraction (fnn) of a component having the second spin-spin relaxation time being less than 0.2, as measured at 150°C by Hahn-echo method using pulsed NMR technique.

[Claim 8] The carbon fiber composite material as defined in any one of claims 1 to 7, wherein the flow temperature of the elastomer in the uncrosslinked form is 20°C or more higher than the inherent flow temperature of the elastomer itself.

10 [Claim 9] The carbon fiber composite material as defined in any one of claims 1 to 8, wherein the carbon nanofiber has an average diameter of 0.5 to 500 nm.

[Claim 10] A process for producing a carbon fiber composite material, comprising a step of dispersing carbon nanofibers into an elastomer by shear force, wherein the elastomer has an unsaturated bond or a group, having affinity to the carbon nanofiber.

15 [Claim 11] The process for producing a carbon fiber composite material as defined in claim 10, wherein the elastomer has an average molecular weight is 5,000 to 5,000,000.

[Claim 12] The process for producing a carbon fiber composite material as defined in claim 10 or 11, wherein the elastomer has, in at least one of its main chain, side chains and terminal chains, at least one functional group selected from functional groups such as a double bond, a triple bond, alpha-hydrogen, a carbonyl group, a carboxyl group, a hydroxyl group, an amino group, a nitrile group, a ketone group, an amido group, an epoxy group, an ester group, a vinyl group, a halogen group, a urethane group, a biuret group, an allophanate group and a urea group.

25 [Claim 13] The process for producing a carbon fiber composite material as defined in any one of claims 10 to 12, wherein the elastomer has a spin-spin relaxation

time (T_{2n}) of its network component of 100 to 3,000 microseconds in its uncrosslinked form as measured at 30°C by Hahn-echo method using pulsed NMR technique.

[Claim 14] The process for producing a carbon fiber composite material as defined in any one of claims 10 to 13, wherein the carbon nanofibers have an average
5 diameter of 0.5 to 500 nm.

[Claim 15] The process for producing a carbon fiber composite material as defined in any one of claims 10 to 14, wherein the step of dispersing carbon nanofibers into an elastomer by shear force is carried out in accordance with an open-roll method using the roll spacing of 0.5 mm or less.

10 [Claim 16] The process for producing a carbon fiber composite material as defined in claim 15, wherein two rolls used in the open-roll method have surface velocity ratio of 1.05 to 3.00.

[Claim 17] The process for producing a carbon fiber composite material as defined in any one of claims 10 to 14, wherein the step of dispersing carbon nanofibers
15 into an elastomer by shear force is carried out in accordance with a closed kneading method with a rotor spacing of 1 mm or less.

[Claim 18] The process for producing a carbon fiber composite material as defined in any one of claims 10 to 14, wherein the step of dispersing carbon nanofibers into an elastomer by shear force is carried out in accordance with a multi-axis extruding
20 kneading method with a screw spacing 0.3 mm or less.

[Claim 19] The process for producing a carbon fiber composite material as defined in any one of claims 10 to 18, wherein the step of dispersing carbon nanofibers into an elastomer by shear force is carried out at a temperature of 0 to 50°C.

[Claim 20] The process for producing a carbon fiber composite material as
25 defined in any one of claims 10 to 19, further comprising a step of crosslinking the elastomer after the step of dispersing carbon nanofibers into an elastomer by shear force.

[Title of the Document] SPECIFICATION

[Title of the Invention] CARBON FIBER COMPOSITE MATERIAL AND
PROCESS FOR PRODUCING THE SAME

[Technical Field]

5 The present invention relates to a carbon fiber composite material and a process
for producing the same.

[Background Art]

 In recent years, composite materials using carbon nanofibers have been focused.
Such composite materials are expected to having improved mechanical strength owing
10 to the incorporation of a carbon fiber. Since the carbon nanofibers have a strong
mutually aggregating property, however, it is considered to be very difficult to
homogeneously disperse the carbon nanofibers into a substrate of composite material.
Therefore, it is currently difficult to obtain a composite material of carbon nanofibers
having the desired properties and also it is impossible to use expensive carbon
15 nanofibers efficiently.

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

 It is thus an object of the present invention to provide a carbon fiber composite
material including carbon nanofibers homogeneously dispersed therein and a process of
20 producing such a carbon fiber composite material.

[Means for Solving the Problems]

 A carbon fiber composite material according to the present invention comprises
an elastomer and carbon nanofibers dispersed in the elastomer, wherein the elastomer
has an unsaturated bond or a group, having affinity to the carbon nanofiber.

25 In the carbon fiber composite material of the present invention, the unsaturated
bonds or groups of the elastomer bond with active parts of the carbon nanofibers and
particularly the terminal radicals of the carbon nanofibers to weaken the aggregating

force of the carbon nanofibers, resulting in improvement of its dispersibility. As a result, the carbon fiber composite material of the present invention can have a structure that the carbon nanofibers are homogeneously dispersed in the elastomer as a substrate.

5 The elastomer in the present invention may be either of a rubber system elastomer or a thermoplastic elastomer. In the case of the rubber system elastomer, the elastomer may be either of a crosslinked or uncrosslinked form. As a starting elastomer, the rubber system elastomer may be used in an uncrosslinked form.

10 The carbon fiber composite material according to the present invention may comprise an elastomer and carbon nanofibers dispersed in the elastomer, wherein a first spin-spin relaxation time (T_{2n}) in its uncrosslinked form is 100 to 3,000 microseconds and a second spin-spin relaxation time (T_{2nn}) being zero or 1,000 to 10,000 microseconds, the fraction (f_{nn}) of a component having the second spin-spin relaxation time being less than 0.2, as measured at 150°C by Hahn-echo method using pulsed NMR technique.

15 Further, the carbon fiber composite material according to the present invention may comprise an elastomer and carbon nanofibers dispersed in the elastomer, wherein a first spin-spin relaxation time (T_{2n}) in its uncrosslinked form is 100 to 3,000 microseconds and a second spin-spin relaxation time (T_{2nn}) is absent or 1,000 to 10,000 microseconds, the fraction (f_{nn}) of a component having the second spin-spin relaxation time being less than 0.2, as measured at 150°C by Hahn-echo method using pulsed NMR technique.

The carbon fiber composite material of the present invention has such properties and a structure that the carbon nanofibers are homogeneously dispersed in the elastomer as a substrate.

25 The process of producing a carbon fiber composite material according to the present invention comprises a step of dispersing carbon nanofibers into an elastomer by shear force, wherein the elastomer has an unsaturated bond or a group, having affinity to

the carbon nanofiber.

According to the process of the present invention, the carbon nanofibers can be very well dispersed in the elastomer. This can also provide a carbon fiber composite material in which the dispersibility and stability of the carbon nanofibers is improved.

5 The step of dispersing carbon nanofibers into an elastomer by shear force may be carried out by using, for example, any one of:

(a) an open-roll method with a roll spacing of 0.5 mm or less;

(b) a closed kneading method with a rotor spacing of 1 mm or less; and

(c) a multi-axis extruding kneading method with a screw spacing of 0.3 mm or
10 less.

[Best Mode for Carrying out the Invention]

One embodiment of the present invention will now be described in detail with reference to the attached drawings.

The production process according to this embodiment comprises a step of
15 dispersing a carbon nanofiber into an elastomer by shear force, wherein the elastomer having an unsaturated bond or a group, having affinity to the carbon nanofibers.

It is desirable that the elastomer has such features as having a certain length of molecule, being flexible and others in addition to its higher affinity to the carbon nanofibers. It is also desirable that the step of dispersing a carbon nanofiber into an
20 elastomer by shear force includes kneading by as high shear force as possible.

(a) The elastomer will be first described.

The molecular weight of the elastomer is preferably in the range of 5,000 to 5,000,000 and more preferably of 20,000 to 3,000,000. If the molecular weight of the elastomer is in this range, the elastomer molecules get tangled together and
25 interconnected to one another. Thus, the elastomer tends to enter the aggregated carbon nanofibers easily, resulting in improved separation of the carbon nanofibers. If the molecular weight of the elastomer is smaller than 5,000, however, the molecules of the

elastomer cannot be sufficiently intertwined with one another. This reduces the effect of dispersing the carbon nanofibers even if the elastomer is subjected to shearing force in the subsequent step. If the molecular weight of the elastomer is larger than 5,000,000, the elastomer is hardened too much, making it difficult to be worked.

5 In the elastomer, a spin-spin relaxation time ($T_{2n}/30^{\circ}\text{C}$) of its network component in its uncrosslinked form, as measured at 30°C by Hahn-echo method using pulsed NMR technique is preferably 100 to 3,000 microseconds and more preferably 200 to 1,000 microseconds. By having such a spin-spin relaxation time in the
10 aforementioned range ($T_{2n}/30^{\circ}\text{C}$), the elastomer can be flexible to provide a sufficiently high molecular mobility. As a result, the elastomer can easily enter the interspaces of the carbon nanofibers under its high molecular mobility when the carbon fibers are mixed into the elastomer. If the spin-spin relaxation time ($T_{2n}/30^{\circ}\text{C}$) is shorter than 100 microseconds, the elastomer cannot have a sufficient molecular mobility. If the spin-spin relaxation time ($T_{2n}/30^{\circ}\text{C}$) is longer than 3,000 microseconds, the elastomer
15 tends to flow as a liquid. This makes the dispersion of carbon nanofibers in the elastomer difficult.

 In the elastomer, a spin-spin relaxation time (T_{2n}) of its network component in its crosslinked form as measured at 30°C by Hahn-echo method using pulsed NMR technique is 100 to 2,000 microseconds. The reason is similar to that in the case of
20 uncrosslinked form. That is, the spin-spin relaxation time (T_{2n}) in the resulting crosslinked elastomer is substantially within the aforementioned range when the uncrosslinked elastomer having the above conditions is crosslinked according to the process of the present invention.

 The spin-spin relaxation time obtained by Hahn-echo method using the pulsed
25 NMR technique is a scale representing the molecular mobility of material. More particularly, when the spin-spin relaxation time of the elastomer is measured by Hahn-echo method using the pulsed NMR technique, a first component having a first,

shorter spin-spin relaxation time (T_{2n}) and a second component having a second, longer spin-spin relaxation time (T_{2nn}) are detected. The first component corresponds to a high molecular network component (frame molecule) and the second component corresponds to a high molecular non-network component (the side component such as terminal chains). It can be thus said that the shorter the first spin-spin relaxation time is, the lower the molecular mobility is and the harder the elastomer is. It can be further said that the longer the first spin-spin relaxation time is, the higher the molecular mobility is and the softer the elastomer is.

The measurement using the pulsed NMR technique may be carried out by solid-echo method, CPMG (Car-Purcel-Meiboom-Gill) method or 90° pulse method rather than Hahn-echo method. However, Hahn-echo method is suitable for the present invention since the carbon fiber composite material according to the present invention has a moderate spin-spin relaxation time (T_2). Generally, the solid-echo method and 90° pulse method are suitable for the measurement of a shorter T_2 , the Hahn-echo method is suitable for the measurement of a moderate T_2 and the CPMG method is suitable for the measurement of a longer T_2 .

The elastomer has, in at least one of its main chain, side chains and terminal chains, an unsaturated bond or group having affinity for carbon nanofibers and particularly their terminal radicals, or has a property tending to produce such radicals or such a group. The unsaturated bond or group is at least one of functional groups such as a double bond, a triple bond, alpha-hydrogen, a carbonyl group, a carboxyl group, a hydroxyl group, an amino group, a nitrile group, a ketone group, an amido group, an epoxy group, an ester group, a vinyl group, a halogen group, an urethane group, a biuret group, an allophanate group and a urea group.

The carbon nanofiber is usually constituted by six-membered rings of carbon atoms at the side surface thereof and has a closed structure by a five-membered ring introduced at the forward end thereof. However, it is of forced structure in which a

defect may easily occur. Thus, a radical or a functional group tends to form at that part. In this embodiment, the elastomer can be bonded to the carbon nanofibers since the elastomer has, in at least one of its main chain, side chains and terminal chains, has an unsaturated bond or group having a high affinity (reactivity or polarity) to the radical of the carbon nanofiber. As a result, the dispersion of the carbon nanofibers can be facilitated by overcoming the cohesive force of the carbon nanofibers.

The elastomer may be any one of elastomers such as natural rubber (NR), epoxidized natural rubber (ENR), styrene-butadiene rubber (SBR), nitrile rubber (NBR), chloroprene rubber (CR), ethylene propylene rubber (EPR, EPDM), butyl rubber (IIR), chlorobutyl rubber (CIIR), acrylic rubber (ACM), silicone rubber (Q), fluorine-containing rubber (FKM), butadiene rubber (BR), epoxidized butadiene rubber (EBR), epichlorohydrin rubber (CO, CEO), urethane rubber (U) and polysulfide rubber (T); thermoplastic elastomers such as olefinic-based elastomers (TPO), polyvinyl chloride-based elastomers (TPVC), polyester-based elastomers (TPEE), polyurethane-based elastomers (TPU), polyamide-based elastomers (TPEA) and polystyrene-based elastomers (SBS); and mixtures thereof.

(b) Next, the carbon nanofibers will be described.

The carbon nanofibers preferably have an average diameter of 0.5 to 500nm. The carbon nanofibers preferably have an average length of 0.01 to 1000 micrometers.

The amount of mixed carbon nanofibers is not particularly limited and can be set depending on the intended application. The carbon fiber composite material according to this embodiment can use a crosslinked elastomer, an uncrosslinked elastomer or a thermoplastic polymer as an elastomer material without any preliminary treatment or as a starting material for resinous composite materials. If the carbon fiber composite material of this embodiment is to be used as a starting material for metallic or resinous composite materials, it can include the carbon nanofibers in the rate of 0.01 to 50 % by weight. Such a starting material for metallic or resinous composite materials can be

used as a so-called masterbatch which is used as a supply source of carbon nanofibers on mixing carbon nanofibers into a metal or resin.

The carbon nanofibers may include so-called carbon nanotubes and the like. The carbon nanotube has a mono-layer structure in which a graphene sheet of a carbon
5 hexagonal network is closed into a cylindrical form or a multi-layer structure in which these cylindrical structures are arranged in a nested form. That is, the carbon nanotube may be of the mono-layer structure alone or of the multi-layer structure alone, or may comprise a mixture of the mono-layer structure and the multi-layer structure. A carbon material partially having a structure of carbon nanotube can be also used. In this regard,
10 the carbon nanotube is sometimes referred to as the name of graphite fibril nanotube.

The mono-layer or multi-layer carbon nanotube can be produced into the desired size by the arc discharge method, the laser abrasion method, the vapor-phase growth method or the like.

The arc discharge method is a method wherein arc-discharge is conducted
15 between electrode materials made of carbon rods under an argon or hydrogen atmosphere having a pressure slightly lower than the atmospheric pressure to obtain a multi-layer carbon nanotube deposited on the negative electrode. Further, the mono-layer carbon nanotube can be obtained from soot attached onto the inside surface of a processing vessel by conducting arc-discharge using carbon rods into which a
20 catalyst such as nickel/cobalt is mixed.

The laser abrasion method is a method wherein a target carbon surface mixed with a catalyst of nickel/cobalt is irradiated with a strong pulse laser beam of YAG laser in an atmosphere of noble gas (e. g. argon) to melt and evaporate the carbon surface, resulting in provision of a mono-layer carbon nanotube.

25 The vapor-phase growth method is a method wherein hydrocarbons such as benzene or toluene are thermally cracked in a gas phase to synthesize carbon nanotubes. More particularly, the flow catalytic method, zeolite carrying catalytic method can be

exemplified.

The carbon nanofiber may be improved in adhesion and wettability to the elastomer by kneading with the elastomer after any surface treatment including ion injecting, sputter etching, plasma or other treatments has been previously carried out to the carbon nanofiber.

(c) Thirdly, a step of dispersing the carbon nanofibers into the elastomer by shear force will be described.

In the this embodiment, the step of dispersing the carbon nanofibers into the elastomer is carried out by an open-roll method with a roll spacing equal to or less than 0.5 mm.

Fig. 1 is a schematic view illustrating an open-roll method with two rolls. In Fig. 1, reference numeral 10 denote a first roll and 20 a second roll. The first roll 10 is disposed spaced apart from the second roll 20 by a predetermined spacing d which is preferably equal to or less than 0.5 mm and more preferably 0.1 to 0.3 mm. The first and second rolls are rotated in forward or reverse direction. In the illustrated example, first and second rolls 10, 20 are rotated in directions as shown by arrows, respectively. Assuming that the surface velocity of the first roll 10 is V_1 and the surface velocity of the second roll 20 is V_2 , it is preferred that a ratio between the surface velocities of these two rolls (V_1/V_2) is 1.05 to 3.00. The desired shear force can be provided by using such a ratio of surface velocity. The shear force in this step is suitably set depending on the type of used elastomer, the amount of carbon nanofibers used and the like.

In order to provide as high shear force as possible in this process, further, the mixing of the carbon nanofibers with the elastomer is carried out at a temperature of preferably 0 to 50°C and more preferably 5 to 30°C. With the open-roll method, it is desirable to set the temperature of the roll within the aforementioned range.

If an elastomer 30 is wound around the second roll 20 while the first and second

rolls 10, 20 are being rotated, a so-called bank 32 is formed by the accumulated elastomer between the rolls 10 and 20. Carbon nanofibers 40 are then added into this bank 32. If the first and second roll 10, 20 continue to be rotated, the carbon nanofibers 40 are mixed with the elastomer 30. Subsequently, the distance between the first and second roll 10, 20 is reduced to the aforementioned spacing d . In such a state, the first and second rolls 10, 20 are rotated at a predetermined ratio of surface velocity. Thus, a higher shear force is applied to the elastomer 30 so that the aggregated carbon nanofibers are separated from one another by the shear force and dispersed in the elastomer 30.

At this time, the elastomer of the this embodiment facilitates the dispersion of carbon nanofibers since it has the aforementioned properties such as molecular form (length), molecular motion, chemical interaction with the carbon nanofibers and others. In such a manner, the present invention can provide a carbon fiber composite material which is superior in dispersibility and dispersion stability (which suppresses the re-aggregation of carbon nanofibers). More particularly, when the carbon nanofibers are mixed into the elastomer, the elastomer having its appropriate molecular length and its high molecular mobility enters the interspaces of carbon nanofibers while at the same time the particular part of the elastomer bonds to the highly active parts of the carbon nanofibers under a chemical interaction. When a strong shear force acts on the mixture of the elastomer and carbon nanofibers in such a state, the movement of the elastomer moves the aggregated carbon nanofibers so that they are separated from one another and dispersed into the elastomer. Additionally, the dispersed carbon nanofibers are prevented from being re-aggregated under the chemical interaction. This can provide a good dispersion stability.

The step of dispersing the carbon nanofibers into the elastomer by shear force may be carried out by the closed kneading method or multi-axis extruding method as already mentioned, rather than the aforementioned open-roll method. In brief, this step

may be performed by any one of the aforementioned methods if the shear force can be applied to the elastomer sufficiently to separate the aggregated carbon nanofibers from one another.

After the step of dispersing and mixing the carbon nanofibers into and with the elastomer (mixture/dispersion), various steps of extruding, molding, crosslinking and others may be carried out in a known manner.

In the mixing/dispersing step for the elastomer and carbon nanofibers or after this mixing/dispersing step, a compounding agent used when such an elastomer such as rubber is to be processed may be usually added into the mixture. The compounding agent may be any one of various known compounding agents. For example, the compounding agents may include a crosslinking agent, a vulcanizing agent, a vulcanization accelerator, a vulcanization retardant, a softening agent, a plasticizer, a hardening agent, a reinforcing agent, a filler, an anti-aging agent and a colorant.

(d) Subsequently, a carbon fiber composite material provided by the above method will be described.

In the carbon fiber composite material of this embodiment, the carbon nanofibers are homogeneously dispersed in the elastomer which is a substrate. This means that the elastomer is bound by the carbon nanofibers. In such a state, the mobility of the elastomer bound by the carbon nanofibers is reduced smaller than that of the elastomer not bound by the carbon nanofibers. In the carbon fiber composite material according to this embodiment, therefore, the first spin-spin relaxation time (T_{2n}), the second spin-spin relaxation time (T_{2nn}) and a spin-lattice relaxation time (T_1) become shorter than those of the elastomer alone containing no carbon nanofiber. In this regard, the spin-lattice relaxation time (T_1) in a crosslinked form varies in proportion to the mixed amount of carbon nanofibers.

It is further expected that when the molecules of the elastomer are bound by the carbon nanofibers, the non-network components (non-mesh chain components) decrease

for the following reasons. That is, when the molecular mobility of the elastomer is lowered as a whole by the carbon nanofibers, the parts of the non-network component which cannot easily move increase, these parts tending to behave as in the network. Since the non-network components (terminal chains) are easy to move, they tend to be
5 absorbed by the active points of the carbon nanofibers. For these reasons, it is expected that the non-network components decrease. Therefore, the fraction (fnn) of the components having the second spin-spin relaxation time becomes smaller than the fraction of an elastomer alone containing no carbon nanofibers.

As will be apparent from the foregoing, it is desirable that the carbon fiber
10 composite material according to this embodiment has measured values within the following ranges, as obtained by the Hahn-echo method using pulsed NMR technique.

Namely, it is preferred that in an uncrosslinked form, the first spin-spin relaxation time (T_{2n}) is in the range of 100 to 3,000 microseconds and the second spin-spin relaxation time (T_{2nn}) is in the range of 1,000 to 10,000 microseconds, as
15 measured at 150°C and further that the fraction (fnn) of the component having the second spin-spin relaxation time is less than 0.2.

It is also preferred that in a crosslinked form, the first spin-spin relaxation time (T_{2n}) is in the range of 100 to 2,000 microseconds and the second spin-spin relaxation time (T_{2nn}) is absent or in the range of 1,000 to 10,000 microseconds, as measured at
20 150 °C and further that the fraction (fnn) of the component having the second spin-spin relaxation time is less than 0.2.

The spin-lattice relaxation time (T_1) measured by the Hahn-echo method using the pulsed NMR technique is a scale representing the molecular mobility of a material as in the spin-spin relaxation time (T_2). More particularly, the shorter the spin-lattice
25 relaxation time of the elastomer is, the lower the molecular mobility is and the harder the elastomer is. And also, the longer the spin-lattice relaxation time of the elastomer is, the higher the molecular mobility is, and the softer the elastomer is.

In the carbon fiber composite material according to this embodiment, it is preferred that a flow temperature as determined by the temperature-dependent measurement of dynamic viscoelasticity is 20°C or more higher than the flow temperature of the starting elastomer alone. In the carbon fiber composite material of this embodiment, the carbon nanofibers are well dispersed in the elastomer. Again, this means that the elastomer is bound by the carbon nanofibers. In such a state, the molecular motion of the elastomer is correspondingly reduced to lower the flowability, in comparison with an elastomer containing no carbon nanofiber. Since the carbon fiber composite material of this embodiment has such a flow temperature characteristic, its temperature-dependency of the dynamic viscoelasticity becomes smaller, resulting in improvement of the heat resistance.

As described, the carbon fiber composite material of this embodiment can be used as an elastomer-based material or as a starting material for metallic or resinous composite materials. Usually, the carbon nanofibers are difficult to disperse into a medium since they are intertwined by one another. If the carbon fiber composite material of the this embodiment is used as a starting material for metallic or resinous composite materials, however, the carbon nanofibers can be easily dispersed into a medium when the starting material is mixed with the medium such as metal or resin since the carbon nanofibers have been already dispersed into the elastomer.

[Example 1]

Several examples according to the present invention will now be described, but it is understood that the present invention is not limited to these examples.

(Examples 1 to 6 and Comparative Examples 1 to 3)

(1) Preparation of samples

A polymer substance shown in Table 1 was kneaded with a predetermined amount of carbon nanofibers by the open-roll method to obtain samples. The samples were treated to prepare uncrosslinked and crosslinked samples in the following

manners.

(a) Preparation of uncrosslinked samples

1) A predetermined amount (100g) of polymer substance (100 part by weight (phr)) shown in Table 1 were placed onto and wound around one of 6-inch open
5 rolls (roll temperature of 10 to 20°C).

2) Such an amount (parts by weight) of carbon nanofibers (described as "CNT" in Table 1) as shown in Table 1 was added into the polymer substance. At this time, the distance between the rolls was set to be 1.5mm.

3) If the carbon nanofibers have been added, the mixture of the polymer
10 substance and carbon nanofibers was removed from between the rolls.

4) The distance between the rolls was then reduced from 1.5mm to 0.3mm before the mixture was added between the rolls and subjected to tight milling. At this time, the ratio of surface velocities in the two rolls was set to be 1.1. The tight milling was repeated ten times.

15 5) The distance between the rolls was set to be a predetermined value (1.1 mm) and the mixture having been subjected to the tight milling was charged and subjected to sheeting.

In this manner, uncrosslinked samples used in Examples 1 to 6 and Comparative Examples 2 and 3 were obtained.

20 As a plasticizer for Comparative Example 1, liquid 2-diethylhexyl phthalate (molecular weight: 391) was used. For Comparative Example 2, ethyl cellulose in a thermoplastic resin was used. Furthermore, as Comparative Example 3, an uncrosslinked sample of a polymer substance (EPDM) containing no carbon nanofiber was obtained in a similar manner, except that no carbon nanofiber was mixed in the
25 above steps 1) to 5).

(b) Preparation of crosslinked samples

The steps 1) to 4) were performed in the same manner as in the uncrosslinked

samples.

5) The rolls were set to have a predetermined distance (1.1 mm). The mixture having been subjected to the tight milling was inserted between the rolls and a predetermined amount of a crosslinking agent (2 parts by weight) was further added into the mixture. Thereafter, the mixture was subjected to sheeting.

6) A sample cut into a mold size was set onto a mold and subjected to press-crosslinking at 175°C and 100kgf/cm² for 20 minutes.

In this manner, crosslinked samples of Examples 1-5 and Comparative Example 3 were obtained. In Example 6, SBS (styrene-butadiene-styrene thermoplastic elastomer) was used as a starting elastomer and no crosslinking was performed. In Comparative Example 1, a liquid polymer substance was used and no crosslinking was made. Further, in Comparative Example 2, a thermoplastic resin was used and also no crosslinking was carried out.

(2) Measurement using pulsed NMR technique

15 The uncrosslinked and crosslinked samples were measured by the Hahn-echo method using pulsed NMR technique. This measurement was performed using "JMN-MU25" manufactured by JEOL Ltd. The measurement was performed under such a condition that the observing nucleus is ¹H, the resonance frequency being 25 MHz and 90° pulse width is 2 microseconds so as to measure a damping curve while changing Pi in the pulse sequence (90°x-Pi-180°x) of the Hahn-echo method. Each of the samples was also measured when it had been inserted into a sample tube to an adequate range of magnetic field. The temperature in the measurement was 150°C. By this measurement, the starting elastomer alone and the uncrosslinked and crosslinked samples of the composite materials were determined with respect to the first second spin-spin relaxation times (T2n, T2nn) and the fraction (fnn) of a component having the second spin-spin relaxation time. The results are shown in Table 1. Additionally, the first and second spin-spin relaxation times (T2n, T2nn) of the uncrosslinked samples were

measured at a temperature of 30°C. The results are also shown in Table 1. For the crosslinked samples of the composite materials, a changed amount of a spin-lattice relaxation time (ΔT_1) per % by volume of carbon nanofiber was determined. The results are shown in Table 1.

5 (3) Measurements of E' (dynamic storage modulus), TB (tensile strength) and EB (elongation at break)

For each of the crosslinked samples of the composite materials, E', TB and EB were measured in accordance with JIS K 6521-1993. These results are shown in Table 1. These characteristics could not be measured for Comparative Example 1 since its
10 sample was liquid. Comparative Example 2 was in an uncrosslinked form. Thus, symbol "*" was attached to the numerical values thereof in Table 1.

(4) Measurement of flow temperature

Flow temperatures of the uncrosslinked samples of the starting elastomer alone and composite materials were measured by the dynamic viscoelasticity measurement
15 (JIS K 6394). More particularly, the flow temperature was determined by applying a sine vibration ($\pm 0.1\%$ or less) to a sample having a width of 5 mm, a length of 40 mm and a thickness of 1 mm and measuring the stress and phase difference δ generated thereby. At this time, the temperature was varied from -70°C to 150°C at an elevation rate of 2°C/min. The results are shown in Table 1. In Table 1, no observation of flowing
20 until 150°C was represented by "150°C or higher".

TABLE 1

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparative Example 1	Comparative Example 2	Comparative Example 3	
Raw material elastomer	Polymer substance	EPDM	EPDM	NR	NBR	SBR	SBS	Polymer plasticizer	Ethylcellulose	EPDM	
	Polar group	Double bond Norbornene	Double bond Norbornene	Double bond	Double bond Nitrile group	Double bond	Double bond	Ester group	Ethoxy group	Double bond Norbornene	
	Average molecular weight	200,000	200,000	3,000,000	200,000	150,000	100,000	391	100,000	200,000	
	Uncrosslinked sample	T2n (30°C) (μsec)	520	520	700	300	400	200	550,000	50	520
T2n (150°C) (μsec)		2,200	2,200	5,500	2,000	2,400	2,100	Unmeasurable	12,000 (one component)	2,200	
T2nn (150°C) (μsec)		16,000	16,000	18,000	14,000	17,000	10,000			16,000	
fnn (150°C)		0.405	0.405	0.381	0.133	0.286	0.653			0.405	
Flow temperature (°C)		55	55	40	75	35	100	Liquid	65	55	
Composition	Polymer substance (phr)	100	100	100	100	100	100	100	100	100	
	CNT (phr)	10	60	10	10	10	10	10	10	0	
Composite material	Uncrosslinked sample	T2n (150°C) (μsec)	1,800	1,400	2,000	1,700	2,200	1,500	Unmeasurable	13,000 (one component)	2,200
		T2nn (150°C) (μsec)	6000	None	9,000	9,600	5,600	4,000			180,000
		fnn (150°C)	0.183	0	0.089	0.045	0.171	0.135			0.385
		Flow temperature (°C)	75	150 or higher	100	150 or higher	100	150 or higher	Liquid	70	55
	Crosslinked sample	T2n (150°C) (μsec)	575	620	1,240	597	484	740	Unmeasurable	Not crosslinked	640
T2nn (150°C) (μsec)		3,870	None	3,830	3,380	2,590	3,300	4,150			
fnn (150°C)		0.07	0	0.113	0.088	0.071	0.078	0.117			
E' (30°C) (MPa)		5.86	52.1	2.61	6.9	6.6	12.5	62*	2.98		
TB (MPa)		6.7	25.0	16.6	6.5	4.6	16.2	Unmeasurable	14.5*	1.7	
EB (%)	170	82	170	110	50	160	25*		180		
ΔT1 (msec/CNF 1vol1%)		4.2	6.5	8.3	11.5	7.6	7.2	4	0	0	

From Table 1, the following was confirmed relating to Examples 1 to 6 of the present invention. Namely, the spin-spin relaxation times at 150°C (T_{2n} and $T_{2nn}/150^{\circ}\text{C}$) in the composite materials containing carbon nanofibers (uncrosslinked and crosslinked samples) are shorter than those of the starting elastomer alone containing no carbon nanofiber. Further, the fractions ($f_{nn}/150^{\circ}\text{C}$) of the composite materials containing carbon nanofibers (uncrosslinked and crosslinked samples) are smaller than that of the starting elastomer alone containing no carbon nanofiber. Still further, the spin-lattice relaxation time (T_1) in the crosslinked samples containing the carbon nanofibers is lower than that of the starting elastomer containing no carbon nanofiber by the changed amount (ΔT_1). From these matters, it can be understood that the carbon nanofibers is very well dispersed into the carbon fiber composite material according to the present invention.

This fact is more clearly understood when Examples 1 and 2 are compared with Comparative Example 3. That is, in Comparative Example 3 containing no carbon nanofiber, the spin-spin relaxation times (T_{2n} and $T_{2nn}/150^{\circ}\text{C}$) of the uncrosslinked samples are not so different from those of the starting elastomer alone. On the contrary, in Examples 1 and 2 of the present invention, the spin-spin relaxation times (T_{2n} and $T_{2nn}/150^{\circ}\text{C}$) of the uncrosslinked samples are substantially shorter than those of the starting elastomer alone. In Example 2 wherein the content of the carbon nanofiber is larger, the spin-spin relaxation time ($T_{2nn}/150^{\circ}\text{C}$) of the uncrosslinked samples was not detected. Thus, it has been found that the uncrosslinked samples in Examples 1 and 2 were remarkably different from Comparative Example 3 in respect to T_{2n} and T_{2nn} . It has been also found that there was such a thing in respect to the component fraction ($f_{nn}/150^{\circ}\text{C}$).

It has been confirmed for the crosslinked samples that the spin-spin relaxation times (T_{2n} and $T_{2nn}/150^{\circ}\text{C}$) were those of the starting elastomer alone. Particularly, in

Example 2 wherein the content of the carbon nanofibers is larger, the spin-spin relaxation time ($T_{2n}/150^{\circ}\text{C}$) in the crosslinked samples was not detected. It has been thus confirmed also for the crosslinked samples that Examples 1 and 2 were remarkably different from Comparative Example 3 in respect to T_{2n} and T_{2nn} . Such a thing was
5 similarly confirmed in respect to the component fraction ($f_{nn}/150^{\circ}\text{C}$). Further, the changed amount of the spin-lattice relaxation time (ΔT_1) per % by volume of the carbon nanofiber is all found to be larger values. This indicates that the molecular mobility is lowered as compared with that of the starting elastomer alone.

Still further, from the results of E' , TB and EB using the crosslinked samples, it
10 has been confirmed that the incorporation of carbon nanofibers into the Examples of the present invention improves the dynamic storage modulus and tensile strength while maintaining the elongation at break and that a remarkable stiffening effect is provided by the carbon nanofibers. This can be more clearly understood when Examples 1 and 2 are compared with Comparative Example 3 containing no carbon nanofiber. Particularly,
15 it can be understood that Example 2 wherein the content of the carbon nanofibers is larger has remarkably improved dynamic storage modulus and tensile strength.

Furthermore, since the flow temperature in the composite material (uncrosslinked sample) containing the carbon nanofibers is 20°C or more higher than that of the elastomer alone containing no carbon nanofiber, it can be understood that the
20 composite material has a smaller temperature dependency of dynamic viscoelasticity and an improved thermal resistance.

In Comparative Example 1, the carbon nanofibers were not dispersed since the molecular weight of the elastomer was too small. Further, in Comparative Example 1, the spin-spin relaxation time and properties E' , TB and EB were not measured.

25 In Comparative Example 2, it was confirmed that the carbon nanofibers could not be dispersed sufficiently since the first spin-spin relaxation time (T_{2n}) at 30°C in the starting elastomer was too small. Furthermore, it was still confirmed that the carbon

nanofibers were difficult to be dispersed since the spin-spin relaxation time (T_{2nn}) at 150°C is too large and hence the molecular mobility became too high not to apply the shear force to the samples.

5 In Comparative Example 3, any stiffening effect was found since it contains no carbon nanofibers.

Furthermore, an image of SEM (Scanning Electron Microscopy) for a crosslinked sample of the composite material provided by Example 4 was taken. This SEM image is shown in Fig. 2. The image pick-up condition in this case was selected so that the acceleration voltage was 3.0kV and magnification was 10.0k. It is found from 10 Fig. 2 that the carbon nanofibers are separated from one another and homogeneously dispersed into the substrate of elastomer comprising NBR. In Fig. 2, whitish linear parts indicate carbon nanofibers.

For reference, an image of SEM showing starting carbon nanofibers before mixed is shown in Fig. 3. The image pick-up condition in SEM was selected so that the 15 acceleration voltage was 3.0kV and magnification was 10.0k. It can be understood from the SEM image of Fig. 3 that the starting carbon nanofibers are intertwined with one another.

From the foregoing, it will be apparent that according to the present invention, the carbon nanofibers which would be very difficult to be dispersed into the substrate in 20 the prior art, can be homogeneously dispersed into the elastomer.

[Brief Description of the Drawings]

[FIG. 1] Fig. 1 is a schematic view illustrating the kneading of an elastomer with carbon nanofibers by the open-roll method according to one embodiment of the present invention.

25 [FIG. 2] Fig. 2 is a view showing an image of SEM of a composite material provided according to this embodiment.

[FIG. 3] Fig. 3 is a view showing an SEM image of the starting carbon

nanofibers.

[Explanation of Reference Numerals]

10	First roll
20	Second roll
5 30	Elastomer
40	Carbon nanofiber



2003-309932

[Title of the Document] ABSTRACT

[Abstract]

[Problems] To provide a carbon fiber composite material in which carbon nanofibers are
homogeneously dispersed therein and a process of making such a carbon fiber
5 composite material.

[Solving Means] A carbon fiber composite material includes an elastomer and carbon
nanofibers dispersed in the elastomer, wherein the elastomer has an unsaturated bond or
a group, having affinity to the carbon nanofibers. A process of making the carbon fiber
composite material includes a step of dispersing carbon nanofibers into an elastomer by
10 shear force, wherein the elastomer has an unsaturated bond or a group, having affinity to
the carbon nanofiber.

[Selected Figure] None



FIG. 1

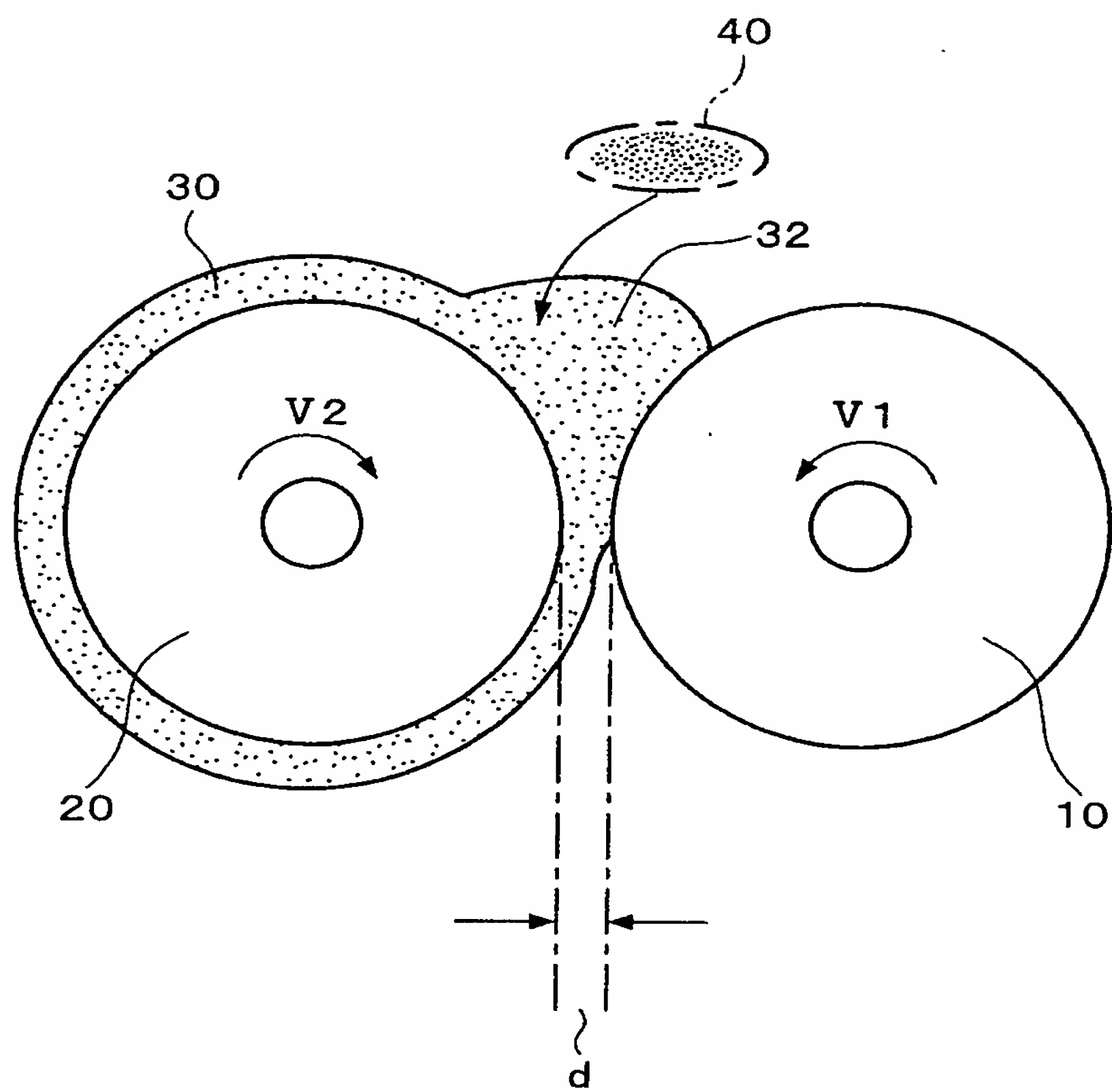


FIG. 2

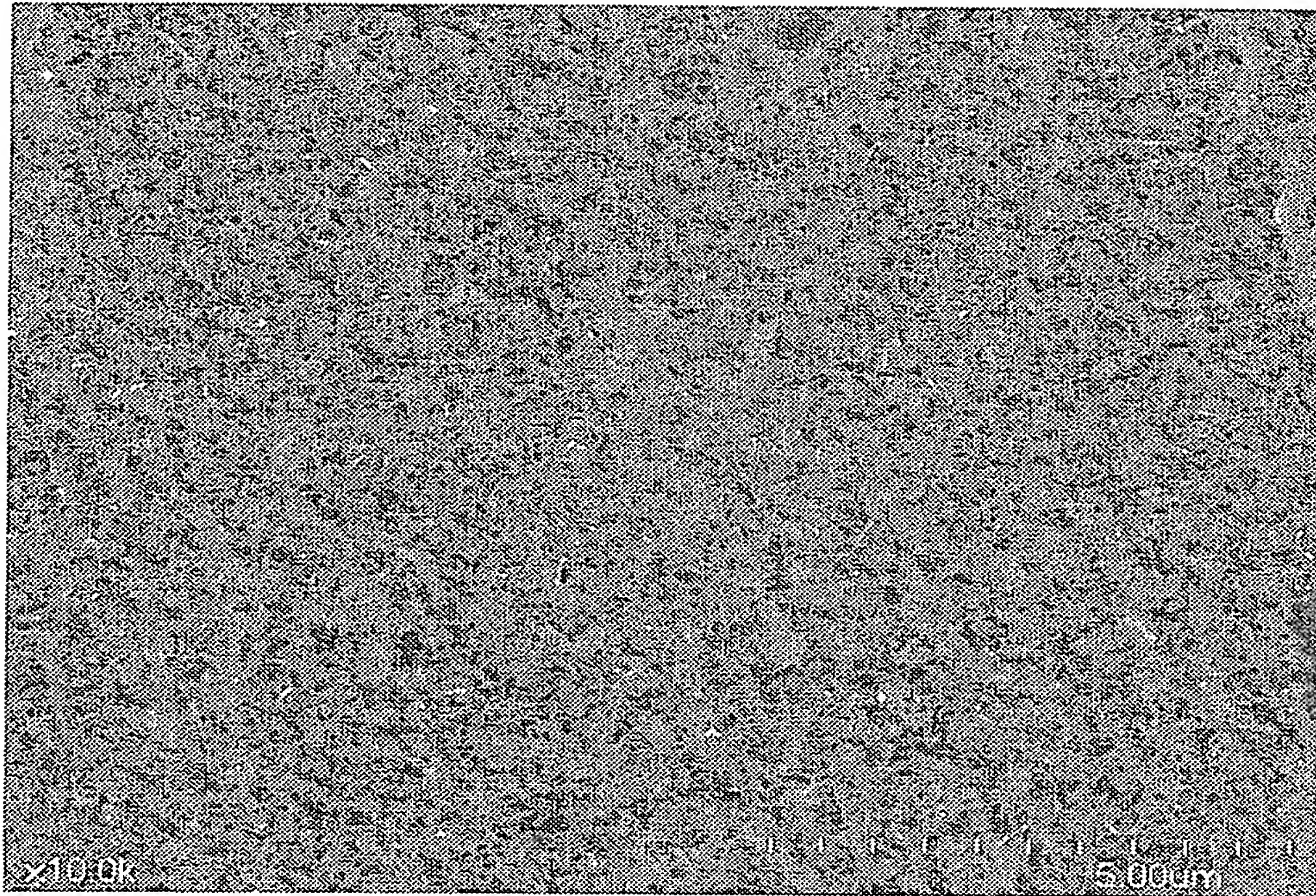


FIG. 3

